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Lithium Ion Solvation and Diffusion in Bulk Organic Electrolytes from First Principles Molecular Dynamics

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INTRODUCTION

Lithium-ion secondary batteries are commonly used to power many consumer devices such as handheld phones, laptops, portable music players, and even electric vehicles. One of the key properties that influence the performance of lithium-ion batteries is the ionic conductivity of the electrolyte (i.e., the movement of Li ions from one electrode to another). This is dependent on the speed at which Li ions diffuse across the cell and related to the solvation structure of the Li ions. The choice of the electrolyte can greatly impact both solvation and diffusivity of Li ions. Many existing batteries use organic liquids to dissolve the Li salt. Commonly used organic liquids in electrolytes can be categorized into linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) or cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC). A good organic solvent will be able to dissolve a high concentration of salt resulting in a high dielectric constant and have a low viscosity to facilitate ionic transport.[1] Often, two or more electrolytes are mixed to optimize these properties and improve battery performance.

To date, there have been many experiments and simulations that have examined the effect of the electrolyte on Li^+ solvation and transport properties. Reported coordination numbers range between 2-5,[2-4] but there has been little experimental work done to characterize the orientation of the solvent molecules around the Li ion. Most recently, NMR experiments have shown that there is a preference for EC to solvate Li^+ in mixed EC/DC electrolyte systems and that carbonyl oxygen atoms are involved in the solvation structure.[5] Experimental diffusion coefficients in different electrolytes range from 1-8 x 10^{-6} cm^2/s at 30°C.[6] Classical potentials have found a coordination number of 4 around Li^+ where carbonyl oxygen atoms of the solvent molecule are arranged in a tetrahedral configuration.[7,8] However, classical potentials are limited in their transferability and the ability to describe charge transfer. These limitations are not present in first principles methods, which can more accurately describe polarizability, charge transfer and partial charges. First principles molecular dynamics simulations were performed previously, which showed good agreement with classical force field results for the solvation structure, but slightly higher values for the diffusion coefficient.[9-11] These works considered systems of ~300-400 atoms and 13-25ps and used certain assumptions such as large hydrogen masses and large time steps. Therefore, it remains unclear how accurately these simulations describe solvation and diffusion in real Li-ion battery systems.

In this work, we use first principles molecular dynamics to examine the solvation and diffusion of lithium ions in the bulk organic solvents ethylene carbonate (EC), ethyl methyl carbonate (EMC), and a mixture of EC/EMC. We find that Li ions are solvated by either carbonyl or ether oxygen atoms of the solvents and sometimes by the PF_6 anion. Li^+ prefers a tetrahedrally-coordinated first solvation shell regardless of which species are involved, with the specific preferred solvation structure dependent on the organic solvent. In addition, we calculate Li diffusion coefficients in each electrolyte, finding slightly larger diffusivities in the linear carbonate EMC compared to the cyclic carbonate EC. The magnitude of the diffusion coefficient correlates with the degree of Li^+ solvation. Corresponding analysis for the PF_6 anion shows greater diffusivity associated with a weakly-bound, poorly defined first solvation shell. Results from this work can be used to design new bulk electrolytes that will improve the performance of current Li-ion batteries.

COMPUTATIONAL METHODS

We performed first principles molecular dynamics using density functional theory (DFT) in the VASP software package.[1] The PBE generalized gradient approximation was used for the exchange correlation functional with Projector Augmented Wave (PAW) potentials. A 450 eV plane-wave cutoff was used and the Brillouin zone was sampled using only the Γ-point. All molecular dynamics simulations were done under NVT conditions since they more closely resemble experimental conditions where the temperature is held fixed. Each system was equilibrated for 5-7.5 ps under NVT conditions at 330 K using a time step of 0.5 fs and a Nose-Hoover thermostat. A temperature of 330K was used in order to ensure that EC is not frozen. This was followed by 30 ps of simulation time under similar conditions as the equilibration in order to gather statistics.

RESULTS AND DISCUSSION

We carried out first principles molecular dynamics simulations to study the effects of several experimentally relevant bulk organic solvents on Li ion solvation and diffusion. The solvation structure for Li^+ in ethylene carbonate has been studied extensively in previous FPMD work, but there is relatively little work reported on the preferred solvation structure in other organic electrolytes with FPMD. We have performed our own first principles molecular dynamics simulations for three different cases: 63 EC + 1 $LiPF_6$, 42 EMC + 1 $LiPF_6$, and 15 EC + 35 EMC + 1 $LiPF_6$. These systems correspond to 638, 638 and 683 total atoms and densities of 1.32, 1.01 and 1.165 g/cc, respectively. In each case, the concentration is approximately 0.22M which is 4-5 times smaller than in commercial batteries. We specifically used 1 Li^+ in these simulations to understand solvation without interaction of other Li ions being present. We performed two independent simulations where the Li^+ and PF_6^- ions are initially associated or dissociated.
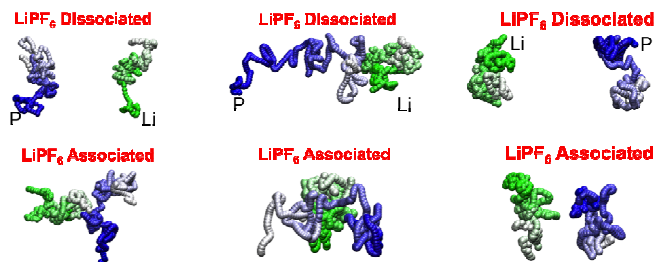

Figure 1. Paths of the trajectories for Li^+ and P atom of PF_6^- for pure EC (left), pure EMC (middle) and EC/EMC mixture (right). Color gradient designates time, where darker colors are early in time.

We first examined the interaction of Li^+ with the counter-ion, PF_6^-. We found that only in the case of EMC does the Li^+ and PF_6^- come back together after they were initially dissociated. For all other cases, the ions either stayed associated or dissociated for the duration of the simulation. In Fig. 1, we show the trajectories for both Li^+ and PF_6^-. In the EC and the mixed EC/EMC case, we found that Li^+ and PF_6^- follow similar trajectories even when they were dissociated by 5-8 Å indicating that their motions are correlated. However, for the EMC case, we observed that the PF_6^- moves toward and finds the Li^+ when initially dissociated. Overall PF_6^- moved more than Li^+, whose motion seems to be confined to a spherical trajectory near its initial position. This is likely due to the Li^+ being more tightly solvated than the PF_6^- in EMC.

We also calculated separate pair correlation functions between the Li ion and both carbonyl oxygen atoms, which we designate O_C, and ethereal oxygen atoms, O_E. We determined that each case results in multiple solvation structures, some of which have yet to be reported in previous theoretical work. The pair correlation functions of Li-O_C and

Li-O$_E$ as well as their integrals for the most energetically favorable solvation structures are shown in Fig. 2. We concluded that solvating Li$^+$ with four carbonyl oxygen atoms is favorable except in the case of pure EMC. The EMC case was the only one where the PF$_6^-$ preferred to remain associated with the Li$^+$. Here, there were 3 carbonyl oxygen atoms solvating the Li$^+$ in addition to the PF$_6^-$. This also suggests that there is a preference for carbonyl oxygen atoms to solvate the Li ion. This is in agreement with previous experimental work performed on mixed EC/DMC systems using ^{17}O NMR.[5] Further examination of the mixed electrolyte case showed that one EMC molecule is removed from the first solvation shell and replaced by an EC molecule resulting in 2 EC molecules and 2 EMC molecules in the first solvation shell. Therefore, this is an indication that there is a strong preference for EC to solvate the Li ion when present, which has been verified experimentally by the NMR work mention above.
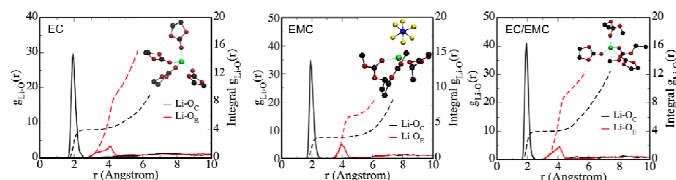
Figure 2. Pair correlation functions (solid) and their integral (dashed) of the most energetically preferred solvation structure for EC, EMC and EC/EMC mixture. A snapshot of the solvation structure is shown in the inset.

We also examined the orientation of the solvent molecules for all three cases. In Fig. 3, we show representative histograms of the O$_C$-Li-O$_C$ bond angle for different solvation structures in each organic solvent where Li$^+$ is solvated with coordination number equal to four. We observed that all have peaks around ~110° indicating that each configuration prefers to have tetrahedral arrangements. The tetrahedral pattern was observed when the Li ion is solvated with four carbonyl oxygen atoms in previous literature for EC. However, we noticed that Li$^+$ seems to prefer a tetrahedral solvation structure regardless of the composition of the first solvation shell. In addition, of all the organic solvents, we found only one solvation structure with a total coordination greater than 4 when including the PF$_6^-$. This non-tetrahedral structure occurred in EMC where the Li$^+$ is solvated by 4 ether oxygen atoms belonging to two EMC molecules and the PF$_6^-$. This structure itself is not energetically preferred and is likely a byproduct of the initial conditions.
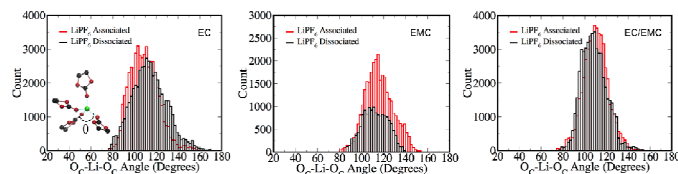
Figure 3. Histogram of the O$_C$-Li-O$_C$ angle for different solvation structures where Li$^+$ is solvated with coordination number of 4. This is plotted for EC, EMC and the EC/EMC mixture. An angle around ~110° indicates that the solvent atoms orient tetrahedrally around Li$^+$. This is defined as θ in the inset.

Finally, we examined the transport properties of the Li$^+$ and PF$_6^-$ ions in each of the different electrolytes by calculating its diffusion coefficient using the Stokes-Einstein relation where the diffusion coefficient can be calculated from the slope of the mean-square displacement as a function of time. In Table 1, the diffusion coefficients calculated for these two ions are listed for each of the electrolytes. Statistical errors for these numbers are about ~1-2 x 10^{-6} cm^2/s or as much as 50%. Improving these errors is nontrivial, as it would require running many independent simulations with one LiPF$_6$ or one simulation with many LiPF$_6$ molecules. The diffusion coefficients vary greatly between different electrolytes, but the highest one was seen for EMC where LiPF$_6$ was initially dissociated. This is in agreement with

experiments where a linear carbonate, such as dimethyl carbonate (DMC), diffuses faster than a cyclic carbonate, such as EC, likely due to its low viscosity.[6] However, Li diffusion in the mixed electrolyte showed slower diffusion than EC when it would be expected to fall between EC and EMC. One trend to notice is that slower diffusion occurs when the Li$^+$ solvation structure is more preferable. Therefore, the magnitude of the diffusion coefficient is strongly dependent on how tightly solvated the Li$^+$ is with its solvent molecules. In addition, PF$_6^-$ shows faster diffusion than Li$^+$ indicating that it is involved in a weaker solvation structure. This consistent with a very broad pair correlation functions that we observed for P-EC compared to Li-EC and calculated residence times that were much shorter than Li$^+$.

Table 1. Calculated Li$^+$ and PF$_6^-$ Diffusion Coefficients

System	D$_{Li}$ (10^{-6} cm^2/s)	D$_P$ (10^{-6} cm^2/s)
EC	5.2 ± 0.8	7.1 ± 0.9
EMC	9.6 ± 1.6	30.8 ± 8.8
3:7 EC:EMC	2.6 ± 1.3	5.7 ± 2.4

CONCLUSION

We found multiple solvation structures for each electrolyte examined with first principles molecular dynamics. Both EC and the EC/EMC mixture show favorable solvation with 4 carbonyl oxygen atoms of the solvent molecules while EMC prefers solvation of 3 carbonyl oxygen atoms and PF$_6^-$. Li$^+$ prefers to be solvated in a tetrahedral configuration regardless of which species are involved, with the specific solvation structure dependent on the organic solvent. We also find large diffusivities for Li$^+$ in linear EMC than cyclic EC in agreement with experiment. The magnitude of the diffusion coefficient correlates with the strength of the Li$^+$ solvation structure. This is also seen in PF$_6^-$, which has larger diffusivities than Li$^+$ due to its weaker solvation structure. Our results suggest that Li$^+$ must have weak interactions with the organic solvent used in the electrolyte to improve mobility. This is valuable insight that can be used to improve the cycling rate of Li-ion batteries and potentially lead to the design of new electrolytes for better overall battery performance.

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